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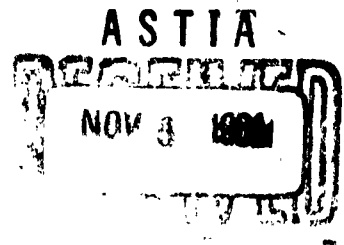ARLINGTON HALL STATION
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ARL 56

RESEARCH ON THE BEHAVIOR OF NEARLY PERFECT CRYSTALS

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GENERAL ELECTRIC RESEARCH LABORATORY
SCHENECTADY, NEW YORK

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(over)

the segregation of a specific impurity to the dislocation sites. Similar etching reagents can be used to reveal dislocations on the (110), (112), and (491) surfaces as well as all surfaces that make an angle of more than 5 degrees with the (100) and (111) planes. However, for these surfaces, it is necessary to decorate the dislocation with an impurity such as carbon. Sufficient decoration for etch pitting is obtained after aging for a minimum of 4 hours at 150°C in a sample containing 0.004 to 0.008 wt per cent carbon.

RESEARCH ON THE BEHAVIOR OF NEARLY PERFECT CRYSTALS

P. D. GORSUCH AND T. H. ALDEN

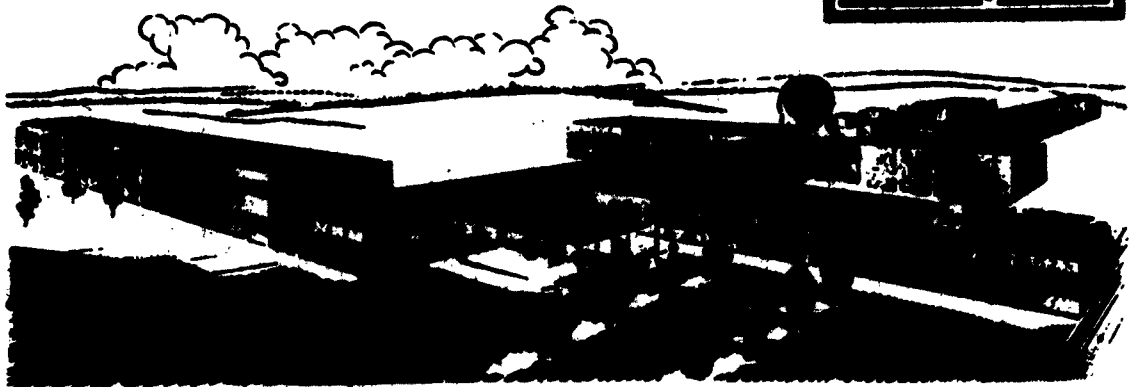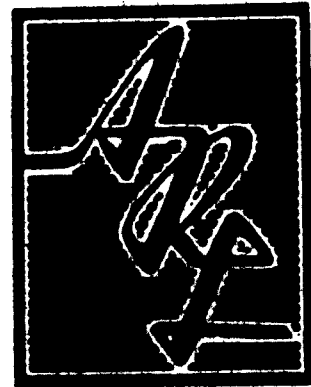*GENERAL ELECTRIC RESEARCH LABORATORY*
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AERONAUTICAL RESEARCH LABORATORY
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UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report covers work carried out in the Metallurgy and Ceramics Research Department of the General Electric Research Laboratory under Air Force Contract No. AF-33(616)-6181, "Research on the Behavior of Nearly Perfect Crystals," Project 7021, "Solid State Research and Properties of Matter," and Task 70627, " Interactions, Imperfections, and Alloy Theory, " and was administered under the direction of the Aeronautical Rsearch Laboratory, Office of Aerospace Research, with Mr. James W. Poynter and Mr Atwell M. Adair acting as project engineers.

This report covers work conducted from December 5, 1958 to December 5, 1960. The authors, Paul D. Gorsuch and Thomas H. Alden, the principal investigators on this project, would like to acknowledge the valuable assistance of J. R. Low, Jr., D. F. Stein, and Miss A. M. Turkalo during the course of this work.

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ABSTRACT

Etching techniques have been developed which are capable of producing etch pits at the intersection of dislocation lines with various crystal surfaces of high-purity single crystals of alpha-iron. For the (100) and (110) surfaces, dislocations can be revealed with or without the segregation of a specific impurity to the dislocation sites. Similar etching reagents can be used to reveal dislocations on the (110), (112) and (491) surfaces as well as all surfaces that make an angle of more than 5 degrees with the (100) and (111) planes. However, for these surfaces, it is necessary to decorate the dislocation with an impurity such as carbon. Sufficient decoration for etch pitting is obtained after aging for a minimum of 4 hours at 150°C in a sample containing 0.004 to 0.008 wt per cent carbon.

The dislocation structure of selected iron whiskers with [100], [110], and [111] growth axes was evaluated using the above etching techniques. There was some qualitative indication that the perfection of the whiskers increases with decrease in whisker diameter and with increase in purity of the halide salt used in their growth. However, the marked variation in dislocation density along the length of a given whisker and between whiskers of a given size range suggests that some feature of the growth process is more important than whisker diameter in establishing crystal perfection. The perfection of whiskers with [111] growth axes tended to be much higher than for those with [100] and [110] growth axes.

In addition to the above techniques for revealing dislocations by etch pits, a method was developed for producing thinned iron whiskers suitable for transmission electron microscopy.

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RESEARCH ON THE BEHAVIOR OF NEARLY PERFECT CRYSTALS

P.D. Gorsuch and T.H. Alden

INTRODUCTION

The remarkable mechanical properties of metal whiskers produced during metal halide decomposition have been known for many years. However, the connection between the structural perfection of whiskers and their strength properties, particularly the reduction in strength with an increase in whisker diameter, is not yet understood. This investigation was undertaken to establish the structural irregularities in metal whiskers as a function of their size in order to more clearly understand the observed mechanical properties.

Early in the investigation it was found that, to study whisker imperfections using etch-pitting techniques, an etch would have to be developed for iron which would reliably disclose dislocation sites. Part I, therefore, is a report of the development of such an etching solution. Part II is a report of the investigation of dislocation structures in iron whiskers using this etching technique.

One of the limitations of these etching methods is the inability to disclose imperfections in whiskers one or two microns and below in size where the strength properties of the whiskers approach theoretical strength values. Part III, is a report on a method whereby small whiskers in this size range may be thinned for examination by electron transmission microscopy.

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PART I

DISLOCATION ETCH PITS IN ALPHA-IRON SINGLE CRYSTALS

P.D. Gorsuch

INTRODUCTION

An etching reagent that produces pits at the intersection of dislocation lines with a crystal surface is an extremely important technique for studying crystal growth and perfection[1] and the role of dislocations in plastic deformation processes.[2] Although techniques have been developed for producing preferential etching at dislocations in a wide variety of both metallic and nonmetallic crystals, very little progress has been made toward developing satisfactory techniques for high-purity iron. However, the preliminary studies of Boswell,[3] Samuel and Quarrell[4] and Lovell, Vogel, and Wernick[5] were useful in indicating the types of reagents to be investigated.

The objective of this research program was to develop a satisfactory procedure for revealing dislocations on various surfaces of high-purity iron single crystals. These techniques were used, in subsequent experiments, to establish the density and distribution of dislocations in "as-grown" iron whiskers as a function of their size and crystal orientation. The results of this latter research will be reported in Part II.

In this study, the following observations were used to justify the conclusion that the etch pits produced under certain specific etching conditions represent the points of emergence of dislocations from the single-crystal surfaces:

1. The etch pits were not distributed in a random pattern, and the density of pits did not vary in a significant manner with etching time.

2. Each etch pit appeared to represent a line defect as shown by repeated polishing and etching of the crystals. For the crystals with a (100) plane of observation, the line defects were also shown to move under stress.

3. The density of pits or the number and width of slip bands increased with increasing amounts of deformation.

4. The qualitative aspects of the substructure were similar to those which hve been observed on other metal single crystals for which dislocation etch-pitting techniques have been developed.

EXPERIMENTAL METHODS

The samples were cut from single crystals of an estimated 99.9 per cent purity iron approximately 0.080 inch thick grown by the strain anneal method by Stein and Low.[6] From the group of 15 crystals which were used in the study, it was possible to find one or more crystals with a plane of sheet orientation within 5 or less degrees of (100), (111), (112) and (491). Other crystals deviated up to about 15 degrees from these planes. The latter crystals were used to evaluate the experimental limitations of each etching reagent.

The surfaces of the crystals were mechanically polished through 000 emery paper followed by either an electropolish in a chromium trioxide-acetic acid bath using the Morris technique[7] or a chemical polish using an oxalic acid-hydrogen peroxide bath. The chemical polishing treatment consisted of:

Solution: 300 cc water
               10 grams oxalic acid
               20 cc hydrogen peroxide (30 per cent solution)

Conditions: 20° to 45°C

Because the mechanical polish distorted the soft iron crystals to a depth of approximately 200 to 300 microns, the latter solution, which is a modification of a bath used to chemically polish steel,[8-10] had an important advantage. At the highest solution temperature about 25 microns of material were removed from the surface per minute as compared to 0.6 for the chrome-acetic bath. Polishing was continued until all traces of surface damage were removed as indicated by the rate of change in pit density with depth. At some point further surface removal did not result in a decrease in the number of pits.

For decoration of the dislocations, the specimens were heated in hydrogen atmospheres containing 1 to 2 per cent methane at 750°C for times ranging from 2 to 4 hours. This treatment increased the carbon content of the material from 0.001 wt per cent or less to a level between 0.004 and 0.008 wt per cent depending upon the methane content of the carburizing atmosphere. The etch pits were, in general, poorly formed or indistinct for aging times of less than 4 hours at 150°C, but additional time had little or no effect.

A few rectangular samples were cut from each crystal for bend tests. The specimen axis orientations were selected so that only one slip system would be favored when they were bent about an axis normal to the long edge of the specimen. Furthermore, the orientations were chosen so that the dislocations produced on the surfaces of observation were varied from being as near screw to as near edge in character as possible. On the (100), (110) and (111) surfaces it was not possible to produce either pure edge or pure screw dislocations because of crystallographic and critical resolved shear stress considerations. However, pure edge dislocations were produced on the (112) and pure screw dislocations on the (491).

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A three-point bending jig was used in the bending experiments. Because of a wide variation in the yield strength between crystals, the samples were progressively loaded in small stress increments with an intermediate short time-holding period. In this way it was possible to limit the magnitude of the plastic strain to about 0.1 per cent. The estimated yield strengths for this strain level were about 4,000 to 6,000 psi for uncarburized and 8,000 to 18,000 psi for carburized specimens.

The rates of dissolution in the various etching solutions were determined by weighing polished crystals before and after immersion in the solutions for 5 minutes. The samples had a minimum surface area of 15 square centimeters to minimize any edge effects, and the solution was mechanically stirred to stimulate the etching procedure.

RESULTS

The procedure used in presenting the results of this experimental investigation is to first tabulate the etching techniques required for each orientation. With this introduction, proof that the surface etch pits represent dislocations can be more easily summarized.

ETCHING REAGENTS

Lovell, Vogel, and Wernick[5] suggested that Fry's reagent was a suitable etching reagent for revealing dislocations in iron as surface etch pits. However, the surface planes on the crystals involved and the etching conditions required were not specified. Some preliminary experiments with the crystals used in this study indicated that this reagent or a suitable modification could be used, under the proper conditions, for reproducibly revealing dislocations on all crystal surfaces. Furthermore, it was found that the appropriate reagent composition for each surface orientation could be qualitatively discussed in terms of the macroscopic rates of dissolution.

The composition of Fry's reagent is:

40 ml concentrated hydrochloric acid

30 ml water

25 ml ethyl alcohol

5 grams cupric chloride

For the purposes of this investigation it was necessary to modify only the cupric chloride concentration of the reagent. The quantity added to the basic solution was varied from zero to the limit of solubility which was approximately 20 grams.
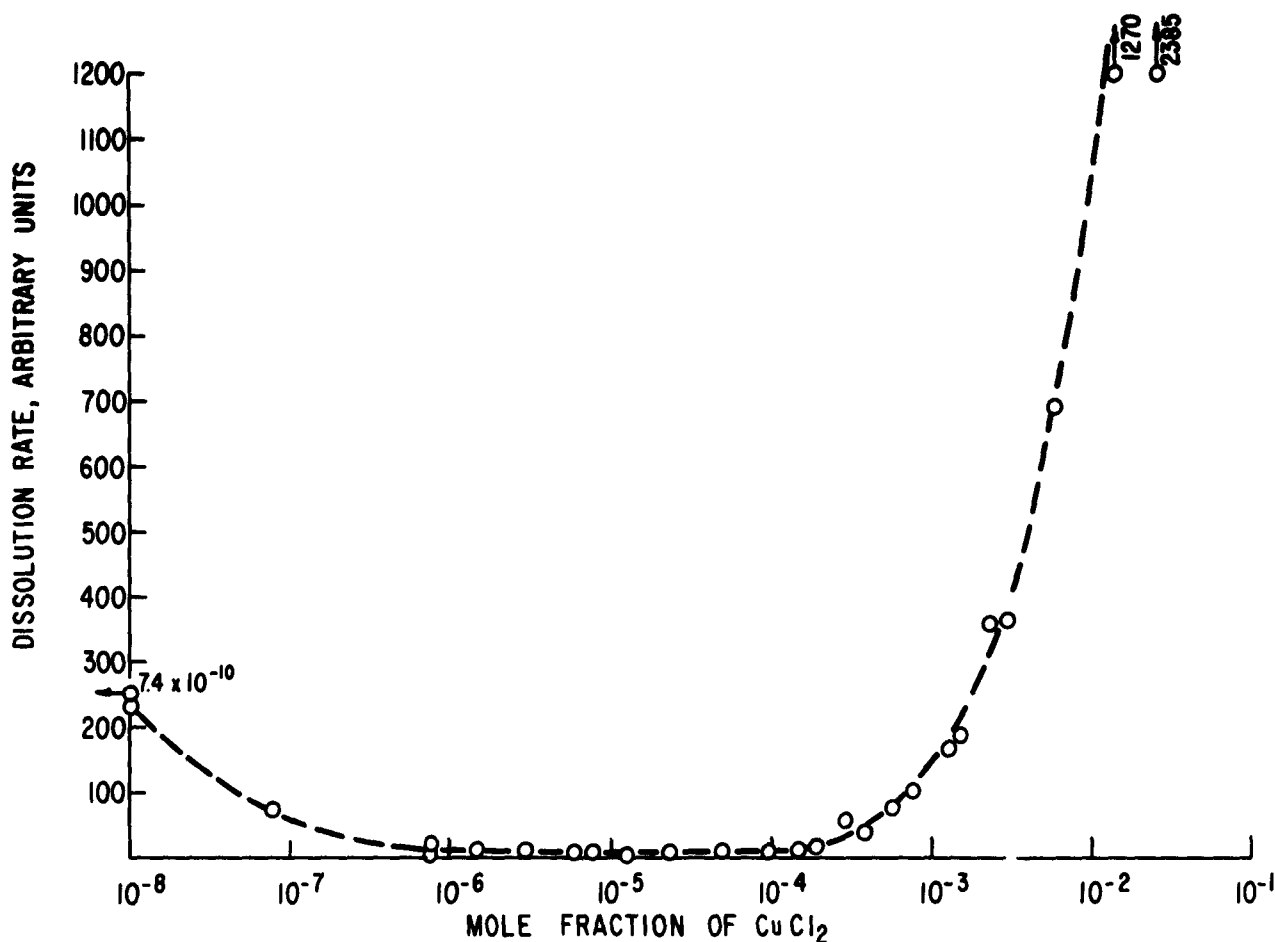
Fig. 1 Rate of dissolution of (112) crystal as a function of $CuCl_2$ content. All points represent an immersion time of 5 minutes.

Figure 1 is a rate of dissolution curves for a crystal with (112) surface planes as a function of the $CuCl_2$ content of Fry's reagent. The data suggest that small concentrations of $CuCl_2$ poison the crystal surfaces and prevent attack by the acid. Higher concentrations, however, appear to catalyze the acid attack. Within experimental error, identical dissolution curves were obtained for the other crystal orientations and are not reproduced. In addition, similar curves were observed when other additives such as Br_2, I_2, $CuBr_2$; CuF_2, $FeCl_3$, and $CuSO_4$ were substituted for $CuCl_2$.

The modification of Fry's reagent that was used for each crystal orientation to produce dislocation etch pits are listed in Table I. The crystals were immersed in the appropriate reagents at room temperature and gently agitated until suitable etch pits were developed. After etching, the specimens were rinsed

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TABLE I

Fry's Reagent Modifications* Used for Revealing Dislocation Etch Pits

Orientation	Carbon Decoration	Optimum Range of $CuCl_2$ Content		Estimated Rate (microns/min)	Etching Time (sec)
		Mol Fraction	Grams		
(100)	No	1.48×10^{-4} to 7.4×10^{-4}	0.1 to 0.5	0.01 to 0.05	10 to 60
(100)	Yes	3.7×10^{-4} to 1.48×10^{-3}	.25 to 2.0	.025 to 1.0	10 to 60
(110)	No	3.7×10^{-3} to 1.11×10^{-2}	2.5 to 7.5	2.5 to 6.0	5 to 30
(110)	Yes	3.7×10^{-4} to 1.11×10^{-2}	0.25 to 7.5	0.025 to 6.0	5 to 60
(111)	Yes	1.48×10^{-3} to 2.96×10^{-2}	10 to 20	7.0 to 15.0	10 to 20
(112)	Yes	3.7×10^{-4} to 2.96×10^{-3}	0.25 to 2.0	0.025 to 1.0	10 to 60
(491)	Yes	3.7×10^{-4} to 2.96×10^{-3}	.25 to 2.0	.025 to 1.0	10 to 60
Surfaces more than 5 degrees off above orientations	Yes	3.7×10^{-4} to 2.96×10^{-3}	.25 to 2.0	.025 to 1.0	10 to 60

*0.2 gram $FeCl_3$ sometimes added to minimize background roughening.

successively in a mixture of 50 per cent concentrated hydrochloric acid and 50 per cent ethyl alcohol, in running tap water and finally in ethyl alcohol (95 per cent). The acid rinse was necessary to minimize staining of the surface with copper during the water rinse.

It is to be noted in Table I that segregation of carbon to the dislocations is a necessary prerequisite for etch-pit formation on all surfaces except the (100) and (110). In addition, the latter surfaces require markedly different rates of dissolution for revealing clean or undecorated dislocations. The manner in which pitting tendency varies with rate of dissolution is illustrated for the (100) surface in Fig. 2. A similar trend can be shown for the (110) surface.

In general, it was found that other additives which produce a change in dissolution rate with concentration of the type indicated by Fig. 1 and which ferrous ions displace from solution could be substituted for $CuCl_2$, Br_2; $CuBr_2$, CuF_2, and $FeCl_3$ were particularly effective. Also, for certain orientations, HBr and HI could be substituted for HCl in the basic solution. As expected there were differences in pit shape and etching rates for the different chemicals. However, the results concerning density and distribution of dislocation etch pits were not sufficiently different than those obtained with the $HCl-CuCl_2$ combination to justify including them in this report.
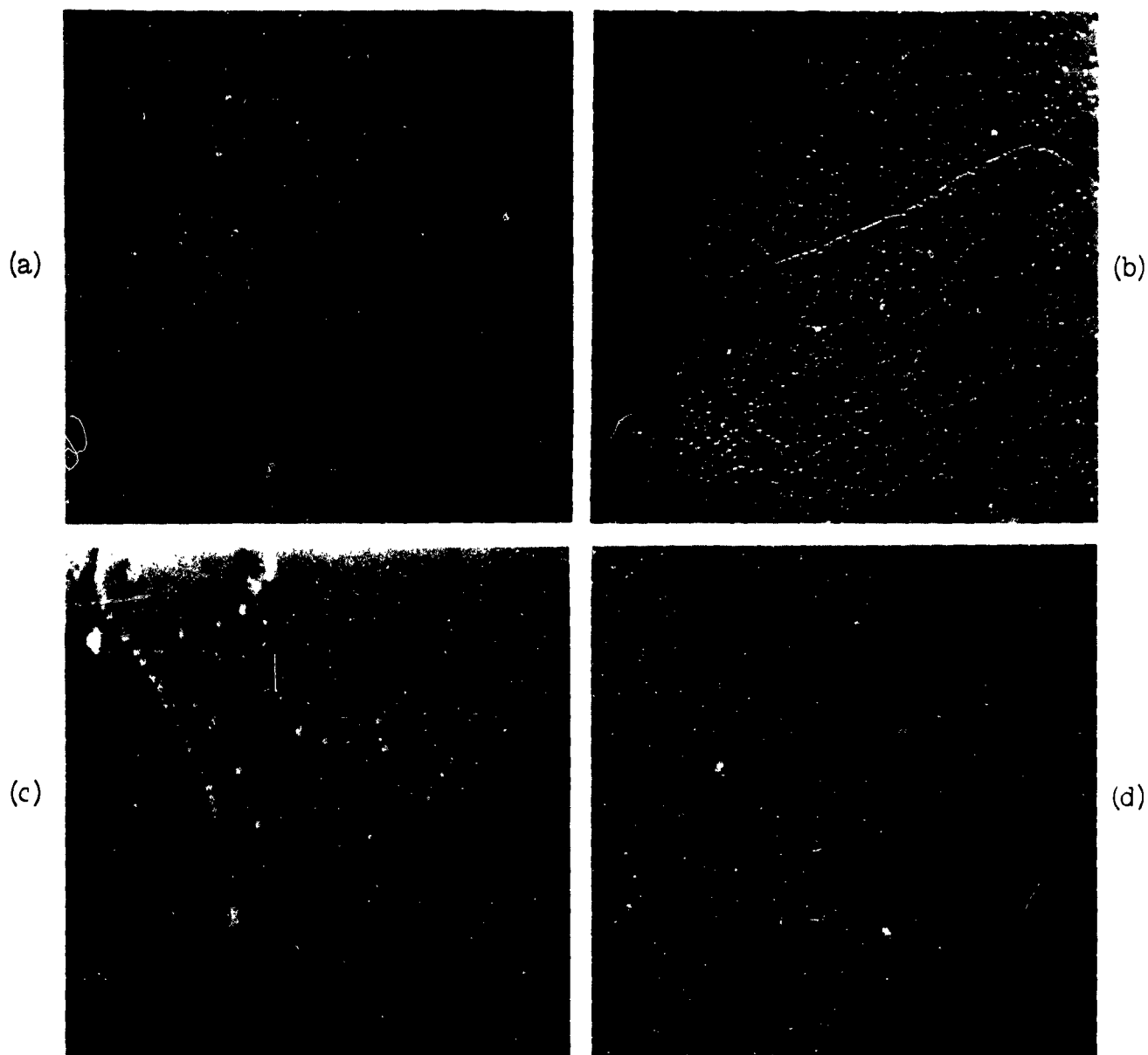
Fig. 2 Effect of CuCl$_2$ concentration in Fry's reagent on tendency to form dislocation etch pits on (100) surface. All crystals were etched 1 minute. (a) No attack--0.01 gram CuCl$_2$. (b) Dislocation etch pits-- 0.1 gram CuCl$_2$. (c) Pits much less distinct--1.0 gram CuCl$_2$. (d) General attack--2.5 grams CuCl$_2$. (Original magnification 1000X. Reduced to 84 per cent.)

Two other etching reagents appear to be equal to or better than Fry's reagent for revealing individual dislocations on the (110) planes. The first reagent consists of:

- 10 ml concentrated hydrochloric acid
- 3 ml concentrated nitric acid
- 100 ml methanol
- 4 grams cupric chloride

In the second reagent, ethyl alcohol is substituted for methanol and 25 grams of picric acid are added. The rate of dissolution is about 3 to 5 microns per minute which is equivalent to that of the appropriate Fry's modification. As with Fry's reagent, it is possible to substitute proper amounts of Br_2, $CuBr_2$, CuF_2 or $FeCl_3$ for the $CuCl_2$.

Alcohol solutions containing 1 to 4 per cent concentrated nitric acid (nital) or 1 to 4 per cent picric acid (picral) were not found to be satisfactory etching reagents as was suggested by the studies of Boswell[3] and Samuel and Quarrell.[4] A few typical results are included, however, for comparison with the results obtained using modifications of Fry's reagent.

Attempts to use the electrolytic etching procedure developed for silicon-iron by Dunn and Daniels[11] were not successful. However, electrolytic etching in either an ethyl alcohol or methyl alcohol solution containing 5 to 20 per cent concentrated hydrochloric acid was found to be useful for all surfaces with carbon decorated dislocations. In particular, this technique could be used to reveal dislocations on both sets of surfaces of a specimen with two different planes of observation. With other reagents, two different treatments with an intermediate polishing treatment were usually required.

(100) PLANE OF OBSERVATION

Repeated etching and alternate polishing and etching were used to show that the surface etch pits follow line defects in the crystals. In addition, it was possible through the use of a double etch technique to show that the line defects move under stress.

Figure 3 illustrates the results of a sequential etching study on a specimen with clean or undecorated dislocations. As the total etching time is increased, the number of etch pits remains essentially constant but the pyramidal shaped pits get broader and deeper. The pit width increases approximately linearly with etching time until the corrosion products build up to such an extent that the etching conditions are modified. Figure 4 illustrates the severe general attack that results from this change. This tendency for over-all attack was minimized by frequent rinses in the HCl-ethyl alcohol solution, but could not be prevented for long etching times.

Fig. 3 Effect of time of etching on density and distribution of etch pits on (100) surface. (a) 1 minute. (b) 2 minutes. Fry's reagent with 0.2 gram $CuCl_2$ and 0.2 gram $FeCl_2$. (Original magnification 1000X. Reduced to 50 per cent.)

Fig. 4 General attack for long etching times. 4 minutes etching in Fry's reagent with 0.5 gram $CuCl_2$. (Original magnification 1000X. Reduced to 50 per cent.)

Repeated polish-etch cycles gave essentially the same pattern in a given area. Some variation was noted due to variations in the geometrical distribution of dislocations with depth, but the differences were not considered to be significant.

Fig. 5 Double etch technique showing dislocation motion. (100) crystal was etched, stressed and re-etched. Fry's reagent with 0.2 gram $CuCl_2$ and 0.2 gram $FeCl_2$. Each etching period was 1 minute. (Original magnification 1000X. Reduced to 50 per cent.)

Figure 5 shows the change in appearance of the etch pits which takes place when the crystal is subjected to a light stress between two immersions in the etching solution. For the first etch the pits were all essentially sharp-bottomed as was illustrated in Fig. 3. After stressing, there are large sharp-bottomed pits, large flat-bottomed pits, and small sharp-bottomed pits. As was discussed by Gilman and Johnston[12] for LiF, the large flat-bottomed pits represent the original positions of the dislocations which moved under stress and the small sharp-bottomed

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pits their final position. The large sharp-bottomed pits show the positions of dislocations that were not moved during the application of the stress.

(a)   (b)

Fig. 6 Increase in pit density with deformation
(a) Undeformed. (b) Deformed to approximately 0.1 per cent plastic strain. Fry's reagent with 0.2 gram $CuCl_2$. (Original magnification 250X. Reduced to 50 per cent.)
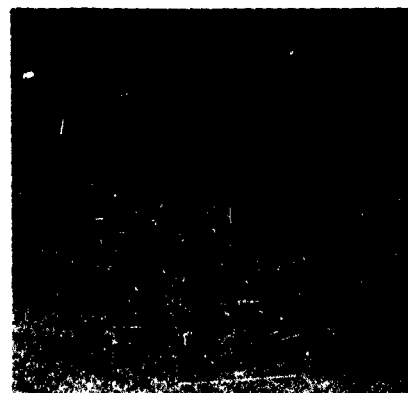
Fig. 7 Slip lines on carburized (100) crystal. Fry's reagent with 0.5 gram $CuCl_2$. (Original magnification 250X. Reduced to 50 per cent.)

Without carbon decoration, the density of pits increased with increasing amounts of deformation (Fig. 6), but no slip bands were formed. Figure 7 illustrates the appearance of slip bands in a carburized specimen bent about an axis perpendicular to its long edge with all surfaces of observation being (100) planes (a cube-oriented sample). Analysis of the angles the slip traces make with each other and with the surfaces of the specimen showed that slip had occurred on (112) planes rather than (110) planes as was observed with all other samples. This observation is consistent with a 15 per cent higher critical resolved shear stress on (112) planes than on the (110) planes. [13]

No etch pits were revealed without carbon decoration when picral etchant was used. Nital produced some tendency for pitting as shown by the small angle boundary in Fig. 8. The difference in diameter of the pits is believed to arise from nonuniform segregation on the dislocation line. The pits become much more uniform in size in a sample slow-cooled from the growth temperature. The rough background in the samples etched in nital can be improved by a subsequent etch in picral as suggested by Boswell. [3] However, without decoration the pits appear to be very shallow and indistinct.

Properly modified Fry's reagent appears to be a satisfactory etch for showing dislocation etch pits when the crystal surface is less than 3 degrees to 5 degrees off the (100) plane. With carbon decoration this can be extended to 10
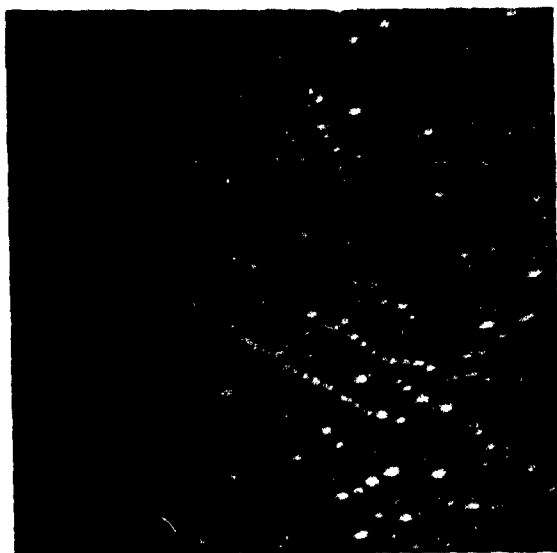
Fig. 8 Small-angle boundary on (100) surface. Two per cent nital. (Original magnification 1000X. Reduced to 80 per cent.)

degrees or more degrees off this plane, but the pits are not as distinct as those on the more perfectly oriented crystals. Segregation of carbon to the dislocation line changes the shape of the pit from pyramidal to conical and increases the rate of attack by a factor of 5 to 10.

(110) PLANE OF OBSERVATION

The continuous nature of the etch pits formed on (110) surfaces was established by repeated etching and by polish-etch cycle both with and without carbon decoration. A typical example of a small-angle boundary and the general background density of pitting is shown in Fig. 9.

Attempts to show that these defects can be moved under stress using the double-etch technique were not successful as shown in Fig. 10. Deformation is accomplished by the generation of new dislocations at the very large pits which represent the former sites of nonmetallic inclusions rather than through the movement of exciting dislocations. The exact reason for this difference in behavior between the (100) and (110) crystals is not known.

As with the (100) crystals, no slip bands were found in deformed samples unless they were carburized. The density of pits did increase, however, with increasing deformation. Figure 11 is a typical example of the slip band formation in crystals which have been carburized. The dislocations in all bands have a mixed edge and screw character.

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Fig. 9 Small-angle boundary on (110) surface. Fry's reagent with 5.0 grams $CuCl_2$ for 15 seconds. (Original magnification 1000X. Reduced to 64 per cent.)
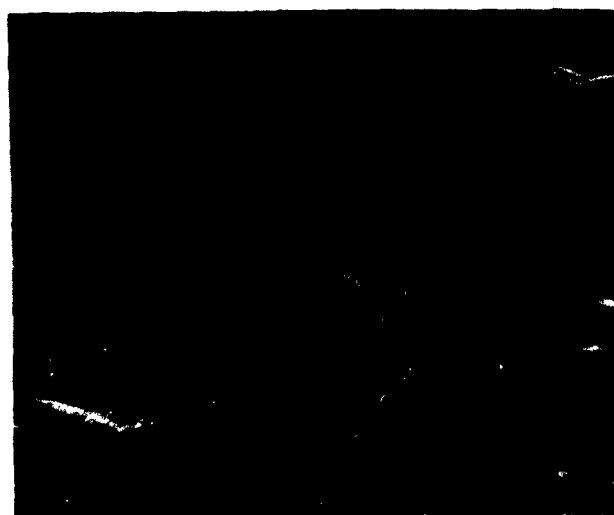
Fig. 10 Double etch technique to show the nucleation of dislocations at inclusions. Fry's reagent with 5.0 grams $CuCl_2$. Etching increments 15 seconds each. (Original magnification 1000X. Reduced to 64 per cent.)

Fig. 11 Slip lines on carburized (110) crystal. Fry's reagent with 5.0 grams $CuCl_2$. (Original magnification 100X. Reduced to 55 per cent.)

Fig. 12 Polygonization in a deformed and annealed (110) crystal. Fry's reagent with 5.0 grams $CuCl_2$. (Original magnification 250X. Reduced to 55 per cent.)

Figure 12 shows an example of the polygonized structure in a sample deformed and annealed for 4 hours at 800°C. Because no simple polygonized structure is developed as a result of deforming and annealing (110) crystals, the excess pit densities created during bending and annealing cannot be compared with the equilibrium dislocation density calculated from the geometry.[14]

The various etching reagents which can be used for the (110) surface were found to be capable of producing satisfactory etch pits for deviations from this plane of at least 10 degrees. An example of the results obtained for a sample oriented 10 degrees off the (110) is shown in Fig. 13. This example shows both the nucleation of dislocations at inclusions and some slip bands that were introduced by accidentally straining the sample during the growth process. In general, decoration did not modify the shape of the pits but did markedly increase the rate of attack.
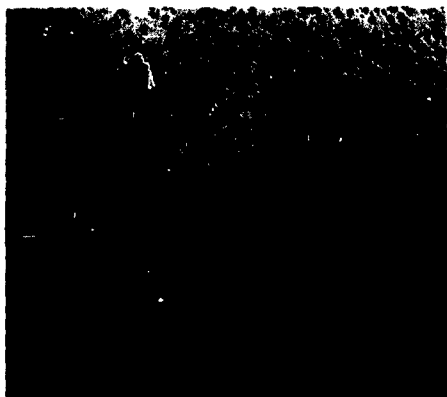
Fig. 13 Etch-pit patterns on crystal 10 degrees off (110). Fry's reagent with 4 grams $CuCO_4$. (Original magnification 250X. Reduced to 50 per cent.)

(111) PLANE OF OBSERVATION

The density of dislocations in the two (111) crystals studied approached 10^8 dislocation lines per square centimeter. This high density made it difficult to establish whether the etch pits represented line defects. For this reason only a few experiments were performed to determine which reagents produced etch pit patterns similar to those observed in the other crystals. Figure 14 shows a typical sub-boundary network which was observed with the proper etching technique.

Of all the orientations studied, the (111) surface was the most difficult to reproducibly etch pit and carbon decoration was a necessary prerequisite. Picral appeared to give the best results, but satisfactory results were obtained with either properly modified Fry's reagent or hydral (5 to 20 per cent concentrated hydrochloric acid in ethyl alcohol) used electrolytically.

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Fig. 14 Substructure in (111) crystal.
Fry's reagent with 20 grams $CuCl_2$.
(Original magnification 500X.
Reduced to 61 per cent.)

(112) PLANE OF OBSERVATION

The various etching reagents were evaluated as to which would reveal (1) the general type of substructure expected for crystals grown by the strain anneal method, (2) dislocations of both edge and mixed character in slip bands, and (3) the polygonized structure in a deformed and annealed specimen. No etching technique was found to be capable of revealing dislocations without segregation of carbon to the dislocation line.

Figure 15 is an example of the type of substructure found in all five specimens which were studied. The dislocation density was so high that no attempt was made to determine whether the pits corresponded to line defects. It was observed, however, that the qualitative aspects of the microstructure did not change with repeated etching or alternate etching and polishing.

Fig. 15 Substructure in (112) crystal.
Fry's reagent with 1.0 gram $CuCl_2$.
(Original magnification 250X. Reduced
to 50 per cent.)

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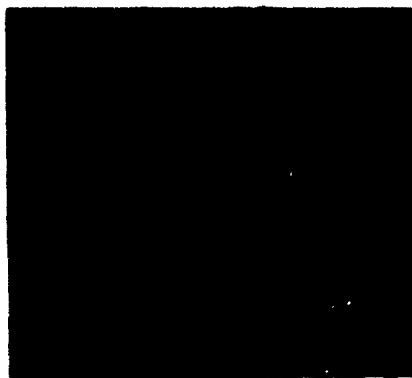
Fig. 16 Slip lines in deformed
(112) crystal. Fry's reagent
with 0.25 gram $CuCl_2$.
(Original magnification 250X.
Reduced to 50 per cent.)

Fig. 17 Polygonization in deformed
and annealed (112) crystal. Fry's
reagent with 0.25 gram $CuCl_2$.
(Original magnification 250X.
Reduced to 50 per cent.)

Slip bands containing pure edge dislocations were obtained by deforming
a specimen about an axis perpendicular to the long edge of the specimen which was
cut with $(1\bar{1}0)$ and $(\bar{1}\bar{1}1)$ planes at 90 degrees to each other and the (112) plane of
observation and at 45 degrees to the axis of the specimen. The results are shown
in Fig. 16. Because more than one slip system was activated, dislocations with
both pure edge and mixed character are illustrated in this one experiment.

Figure 17 shows the classic type of polygonization observed on a sample
deformed to produce edge dislocations and annealed at about 800°C. Unfortunately
the stress system was a combination of bending and tension which is too complex
to be evaluated by the Hibbard and Dunn[14] technique.

Because of the need for carbon decoration, the results were not sensitive
to minor deviations of the crystal surface from the (112) plane. However, the pits
became progressively less sharp and distinct with deviations greater than about
10 degrees.

(491) PLANE OF OBSERVATION

Slip bands containing pure screw dislocations were obtained by deforming
a crystal about a [112] axis perpendicular to the long edge of a specimen with $(11\bar{1})$
and $(1\bar{1}0)$ planes at 90 degrees to each other and the long edge of the specimen and
both at 45 degrees to the (491) plane of observation. The slip bands are illustrated
in Fig. 18. With more than one slip system activated, these results show that both
pure screw and mixed character dislocations can be revealed.
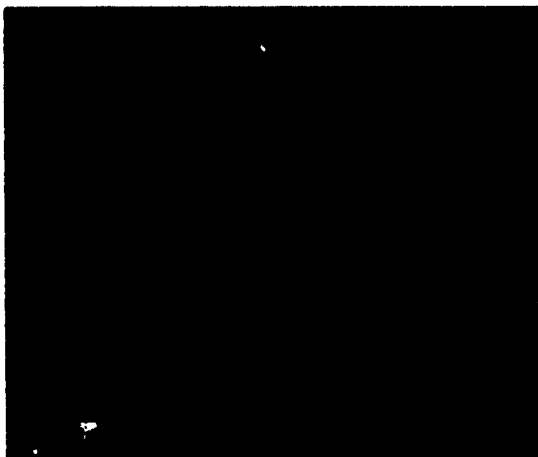
Fig. 18 Slip lines on deformed (491) crystal. Fry's reagent with 0.25 gram $CuCl_2$. (Original magnification 75X. Reduced to 60 per cent.)

As with the (112) specimens, the results were not sensitive to minor deviations of the crystal surfaces from the (491) plane. It was necessary to decorate with carbon to either reveal substructure or deformation dislocations. An aging treatment of 16 hours of 150°C produced more satisfactory results in decorating screw dislocations than did the 4 hours treatment. This is consistent with the observations of Low[15] concerning the relative difficulties involved in decorating edge and screw dislocations in silicon-iron.

POLYCRYSTALS

No single etching technique was found to reveal substructure in all the grains of a polycrystalline sample even with carbon decoration. By varying the composition of Fry's reagent over its extremes and using a variety of etching times, substructure could be revealed in all grains of a carburized and aged sample. The polycrystalline samples were grown by the strain anneal method and had approximately 2-mm-diameter grains.

DISCUSSION

RELIABILITY OF ETCHING REAGENTS

The studies carried out on the single crystals of high-purity iron show that the etch pits are reproducible, do not increase in number with extended etching, are present in densities consistent with those observed in other annealed metals and appear to be line defects as revealed by repeated etching or alternate etching and polishing. Further, the change in nature of the pitting on a (100) specimen when subjected to an applied stress between two immersions in an appropriate etching reagent and the increase in density of pits and formation of slip bands with

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deformation show that these defects can move under stress. Therefore, this seems to be adequate proof that the etching reagents do reveal dislocations by making surface etch pits.

Proof that all dislocations are revealed has not been established. Because of the qualitative similarity of the results on the (100) and (110) surfaces with and without carbon decoration and because deformation dislocations of pure edge, pure screw and mixed character are revealed, it seems probable that most, if not all, of the dislocations are being revealed.

DECORATION OF DISLOCATIONS

The interstitial diffusion of carbon to the dislocation lines is shown to be a necessary prerequisite for producing a preferential attack at dislocation sites for most surface orientations. It is not known whether this simply involves the formation of an impurity atmosphere or whether a second phase particle must be precipitated. The kinetics of carbon precipitation from iron determined by Doremus[16] suggest that the latter process is the most probable.

SLIP BAND FORMATION

The absence of slip bands in (100) and (110) crystals deformed without carburization must result from the fact that either a large number of sources for generating dislocations can be activated at low stresses or the dislocations can readily cross slip. Based on the mechanism for slip band formation suggested by Johnston and Gilman,[17] the latter explanation appears to be the most appropriate. In this hypothesis, slip or glide bands are formed by multiplication, presumably by cross slip, of the first dislocation to move through a given region of a crystal. In a soft crystal the multiplication process would be spread out over great distances in the crystal. This would create the impression that only the density of pits was increased. For a hard crystal, cross slip is difficult and the band formation would be restricted to a relatively narrow region in the crystal. Thus, this gives rise to gross slip bands.

MECHANISM OF DISLOCATION ETCH-PIT FORMATIONS

Cabrera[18] has theoretically considered the phenomena of dislocation etch-pit formation during etching processes. He suggested that a region of undersaturation was needed so that the dissolution would proceed preferentially at dislocations as opposed to perfect surfaces.

Gilman, Johnston, and Sears[19] showed that Cabrera's conclusions must be modified for the preferential etching of dislocations in LiF by a FeF_3 solution. It was insufficient to preferentially create dissolution steps at dislocations. It was also necessary to have a solute present in the etching solution which was adsorbed on the surface and inhibited the motion of steps so that relatively steep visible pits were produced.

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Conclusions concerning the dislocation etch pitting of LiF agree qualitatively with those observed for the etch pitting of undecorated dislocations on the (100) and (110) surfaces of iron. However, the solute added to the iron etching reagent appears to serve a dual purpose since a small but finite rate of dissolution is required [about 0.02 and 3.0 microns for (100) and (110) planes, respectively]. The additive must not only be adsorbed on the surface to control the rate of uniform dissolution but also catalyze the dissolution at the point of emergence of the dislocation.

SUMMARY AND CONCLUSIONS

Fry's reagent or modifications thereof is shown to be a reliable method of revealing dislocations as surface etch pits on the (100), (110), (111), (112) and (491) planes of iron. The segregation of carbon to the dislocation lines is required for preferential etching on all planes except those within 5 degrees or less of the (100) and (110). Dislocations can be revealed on the (100) and (110) planes with or without decoration by carbon.

The formation of etch pits in iron by modifications of Fry's reagent involves the adsorption of $CuCl_2$ on the surface. By varying the concentration of this compound, it is possible to control the relative rates of dissolution step formation at the dislocation sites and the motion of the steps across the crystal. The formation of visible etch pits on the (100) and (110) planes requires a different set of relative rates for these competing processes during the etching procedure. All surfaces need about the same set of conditions when impurities are segregated on the dislocations. This suggests that the rate of dissolution step formation is the controlling factor when impurity segregation to the dislocation lines is involved.

PART II

DISLOCATION ETCH PITS IN IRON WHISKERS

P.D. Gorsuch

INTRODUCTION

A few of the small diameter filaments or "whiskers" grown by the hydrogen reduction of metal halide salts have been shown to have strength properties which approach the high values theoretically predicted for perfect crystals.[20] To exhibit this level of strength, the whiskers must be free from surface defects and not more than a few microns in diameter. Whiskers with gross growth defects and with diameters greater than 10 microns usually approach the same very low strength properties that are characteristic of high-purity metal single crystals. These extreme variations in strength have been attributed to marked differences in the density and distribution of dislocations in the individual whiskers. However, it has not been experimentally demonstrated that such differences in dislocation density do exist between whiskers. It is the purpose of this research program to determine whether the density and distribution of dislocations in iron whiskers can be determined by etch-pitting techniques. If successful, the results were to be correlated with the size, surface perfection and orientation of the whiskers.

Coleman[21] reported that simple etching reagents such as 2 per cent nital (2 per cent nitric acid in ethyl alcohol) and 4 per cent picral (4 per cent picric acid in ethyl alcohol) could be used to reveal dislocations on the (100) surfaces of deformed iron whiskers. Preliminary experiments on the iron whiskers used in this study showed that these etching reagents did not give reproducible results. The distribution and density of etch pits varied drastically with etching time and with repeated polishing and etching. In addition, no pits were found on the surfaces of whiskers which contained small-angle boundaries. The presence of these boundaries was established from rocking curves obtained through the use of a double-crystal x-ray spectrometer.[22]

A program was undertaken, therefore, to develop a satisfactory procedure for reproducibly revealing dislocations on various surfaces of high-purity iron single crystals. The results of this study are now complete,[23] and the techniques developed are used in this study to survey the crystal perfection of iron whiskers.

EXPERIMENTAL METHODS

Hydrogen reduction of $FeCl_2$ and $FeBr_2$ in the temperature range of 700° to 750°C was used to grow a number of boats of iron whiskers.[24] The

composition of the metal halide salts varied qualitatively in the amount and kinds of impurities which were present.

Whiskers with [100], [110] and [111] growth axes were selected from these boats and were etched in alcohol solutions containing 1/2 to 4 wt per cent picric acid or 1 to 4 per cent nitric acid. The diameters of these whiskers ranged from 20 to 200 microns.

Other boats of whiskers were grown and were carburized in hydrogen containing 1 per cent methane at 750°C and were subsequently aged for 16 hours at 150°C. With this procedure and by using the etching techniques developed for revealing carbon-decorated dislocations in iron single crystals, it was possible to reveal only "grown-in" dislocations.

Even with carbon decoration there was a marked tendency for a general attack to take place over the whole whisker surface rather than the selective attack at dislocations as was observed for the iron single crystals. It was found that this effect could be minimized by a series of short-duration immersions in the etching solution with a rinse in a mixture of ethyl alcohol and hydrochloric acid between each immersion rather than the usual single immersion of somewhat longer duration. This suggested that the general attack was associated with a buildup of corrosion products rather than some special chemical behavior of the whisker.

Many etching artifacts were observed due to the tendency for the etching solutions to preferentially attack the edges of the whisker crystals. All of the etching reagents used in the study of the iron single crystals were surveyed to determine their experimental limitations in this regard. The two reagents which were least sensitive to rounding of the edges were selected and used with the carburized sample.

The one etching reagent is essentially a modification of Fry's reagent. It consists of:

> 100 ml ethyl alcohol
> 8 ml concentrated hydrochloric acid
> 1/2 gram   cupric chloride
> Saturate with picric acid

The other reagent, which consists of 5 to 20 per cent hydrochloric acid added to ethyl alcohol, is used electrolytically with a voltage ranging between 1/2 and 2 volts and a current density ranging from about 0.010 to 0.050 milliampere per cm^2. Both solutions give equivalent results and both may be used on (100) and (110) surfaces. Somewhat longer etching times are required for the latter orientations.

RESULTS

Iron whiskers with [100], [110], and [111] growth axes were used in this study. The [100] whiskers are square in cross section and both the side surfaces and the tip were (100) planes. The six faces of the hexagonal shaped [111] fiber axes whiskers are (110) planes. The faces on the tip, however, are (100) planes. The [110] whiskers are rectangular in cross section with the wide faces being (100) planes and the narrow faces (110) planes. The tip of this type of crystal is so poorly defined that indices cannot be assigned. Only the (100) faces were used in the study of the [110] whiskers.

ETCHING WITH NITAL AND PICRAL

Figure 19 illustrates the ability of picral to produce deformation etch pits adjacent to a scratch on the surface of a [100] whisker. Except at the scratch no pits were observed. These results confirm those of Coleman.[21] However, it is not known why this etching reagent will produce etch pits corresponding to undecorated dislocations on the (100) surfaces of whiskers, but not on the (100) surfaces of bulk iron single crystals.[4]

Figure 20 shows a sequential etching experiment at a growth defect on a (100) surface of a [100] fiber axis whisker. It is to be noted that the density and distribution of etch pits does not remain constant with time.

Extended etching of the [110] crystals in picral frequently produced boundaries of what appears to be impurity segregation. This phenomenon is illustrated in Fig. 21. Similar segregation was noted on polished cross sections of some of the large whiskers grown from the halides of lowest purity.

ETCHING OF UNDECORATED WHISKERS

The difficulties encountered in using Fry's reagent or its modification, as was so successful for bulk iron single crystals,[23] is illustrated by the results shown in Fig. 22. Dissolution steps are created at the edges of the crystal which move rapidly across the surface. After the whole surface has been covered by these steps, further etching produces general attack rather than preferential attack at dislocations. In addition, it is not known whether the small pits at the growth bend in the whisker represent an accident of growth or were introduced during removal of the whisker from the boat or in its subsequent handling. For the above reasons, no further studies were made with uncarburized whiskers.

[100] FIBER AXES WHISKERS

The shape of the dislocation etch pit observed on the (100) faces of either the [100] or [110] whiskers is a function of their density. This effect is illustrated

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by Fig. 23. Wherever the dislocation density is high, small conical-shaped pits are formed, but if the density is low there appears to be a dendritic growth of carbide around the carbide core on the dislocation, giving rise to a cross-shaped pit. In Fig. 23, small indents were made in surface of the carburized sample and it was subsequently aged. This, then, is reasonable proof that deformation dislocations are being revealed.

The rapid attack of the etching solutions at the edges of the [100] whisker crystals changes their shape from four-sided to eight-sided. Despite the change in shape, the etching reagents were found to be capable of revealing the dislocations as etch pits on all surfaces. However, the rate of attack is somewhat faster on the edges than on the original surfaces.

Figure 24 illustrates some examples of the wide variation in pit density which was observed along the length of a given whisker and between whiskers of a given size range. It is not possible to illustrate all the results, but the evidence indicates that there might be some tendency for increase in perfection with decreasing whisker diameter down to about 10 microns in diameter. However, the variation within a given whisker and between whiskers of a given size range was much greater than the variation with diameter.

The dislocations were sometimes arranged in low-angle boundaries (Fig. 25). This was particularly true at the tips where the whiskers were frequently accidentally deformed during the growth process (Fig. 26).

Examination of over 40 whisker tips did not indicate any trend in relative perfection of whisker tips and side surfaces. Both tended to have the same degree of perfection for any given whisker. An example of this is shown in Fig. 27.

There seemed to be an indication that the degree of perfection of a crystal increased with depth from the surface. More careful documentation of the results must be carried out before this trend can be proven.

Figure 28 illustrates one of the complex dislocation patterns observed at or near whisker junctions. In some instances, the network extends many whisker diameters away from the junction, but in others only a few dislocations are formed. This probably reflects the degree of misorientation between the two crystals.

Figure 29 shows the dislocation structure of a whisker which was deformed and subsequently annealed at 750°C. The dislocations are tending to array themselves into small-angle boundaries. This is additional evidence that the etchants are revealing dislocations.

(110) FIBER AXIS WHISKERS

The [110] fiber axis whiskers showed extreme variations in crystal perfection. The density of etch pits varied from essentially zero as illustrated by the region away from the growth defect (Fig. 30) to the very high densities shown in Fig. 31. The latter area is adjacent to a point on the crystal where two whiskers intersected and joined during growth. The appearance of the small-angle boundaries is shown in Fig. 32.

The density of dislocations in areas adjacent to growth defects ranged from very low as shown in Fig. 30 to very high as illustrated by Fig. 33.

The polygonized structure in a whisker which was deformed and annealed at 750°C is shown in Fig. 34. As illustrated by the appearance of the crystal at one end of photomicrograph, the original dislocation content was essentially zero.

Surface overgrowths or changes in growth direction are usually accompanied by the presence of dislocations (Fig. 35). There is some evidence for a decrease in dislocation density with depth below the whisker surface. However, the exact correlation could not be established because of the marked variation in dislocation density between crystals.

[111] FIBER AXES WHISKERS

The crystal perfection of this type of whisker is much greater than that for either the [100] and [110] type. Figure 36 illustrates the general level of pit density in most of the whiskers examined. These pits which are present are usually associated in pairs. Sequential etching and repeated polishing and etching were used to establish the fact that they represent closed loop line defects.

Figure 37 illustrates the slip lines observed in a bent crystal, and Fig. 38 shows examples of the low-angle boundaries which were found. Overgrowths of the type illustrated in Fig. 39 is usually accompanied by dislocations of the type illustrated in Fig. 40. Also growth bends were usually a sign of dislocations within the crystal.

A second type of etch pit was produced on some of the crystals. These pits were flat-bottomed and did not represent line defects (Fig. 41). The patterns were retained during repeated polish and etch cycles which suggests that they reflect some condition within the crystal at that point. Impurity segregation seems to be a very probable explanation.

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DISCUSSION

IMPLICATIONS TO CRYSTAL GROWTH THEORY

Attempts to establish whether iron whiskers grow by a screw dislocation mechanism as proposed by Sears[25] for mercury or by the classic coherent two-dimensional nucleation and growth of layers mechanism have been handicapped by a lack of knowledge as to the specific type or types of dislocation structures which exist in the whiskers.[26, 27] Evidence that the whiskers do have dislocations with screw character intersecting surfaces other than the tip would provide strong proof that growth is not controlled by axial screw dislocations.

The results of this investigation show that dislocations do intersect the lateral surfaces of most of the whiskers and that small-angle boundaries may be formed along the length of the whisker and at the junctions between two whiskers which intersect. Despite the fact that some of these dislocations must have screw character, no marked discontinuous lateral growth was observed. However, overgrowths usually, but not always, indicated a region of the whisker which contained dislocations. Thus, it is reasonable to conclude that screw dislocations play a role in controlling the slow radial growth of a whisker but not necessarily the rapid axial growth rates.

The presence of both dislocations and boundaries along the axes of the whiskers is consistent with the postulate that impurities build up in front of the advancing whisker growth interface and are precipitated at periodic intervals. Figure 21 appears to represent experimental proof of this phenomenon. Although the whiskers used in this series of experiments were grown from high-purity materials, these data suggest that improvement in crystal perfection can be achieved by using even higher purity halide salts.

IMPLICATIONS TO STRENGTH MEASUREMENTS

The wide variation in dislocation etch-pit density of the various whiskers can be used to qualitatively explain the great scatter in strength measurements. The data suggest that it would be advantageous to devise methods for growing whiskers with [111] growth axes. This is also the orientation of the strongest whisker tested by Brenner.[20]

SUMMARY AND CONCLUSIONS

Whiskers without obvious growth defects on their surfaces and with [100] and [111] fiber axes tend to be highly perfect with dislocation etch-pit densities ranging from 0 to 10^6 dislocation lines per cm^2. The dislocations are usually arranged in a random manner, but a few small-angle boundaries were observed.

The density of dislocations in [110] fiber axes whiskers varies much more markedly, and there may be extreme variations at any given point along the length of an individual whisker. A few examples were found where a region containing no dislocations was adjacent to a region containing approximately 10^8 dislocation lines per cm^2. There appears to be a marked tendency in the high dislocation density region for the dislocations to arrange themselves in small-angle boundaries.

The appearance of a growth defect on a whisker surface usually but not always indicates a region of the whisker which will contain dislocations.

The boundary between two whiskers which intersect and weld together is usually a very complex dislocation network. The lack of platelet growth at these junctions appears to be further proof that a screw dislocation mechanism is not involved in iron whisker growth.

There is some qualitative indication that the degree of perfection of the whiskers increases with decrease in whisker diameter and with increase in purity of the halide salt used in their growth. However, the marked variation in dislocations density along the length of a given whisker and between whiskers of a given size suggests that some feature of the growth process is more important than whisker diameter in controlling crystal perfection.

The density of dislocations tends to progressively decrease from the surface to the center of a whisker except at growth defects. At growth defects the density of dislocations remains essentially constant throughout the thickness of the whisker.
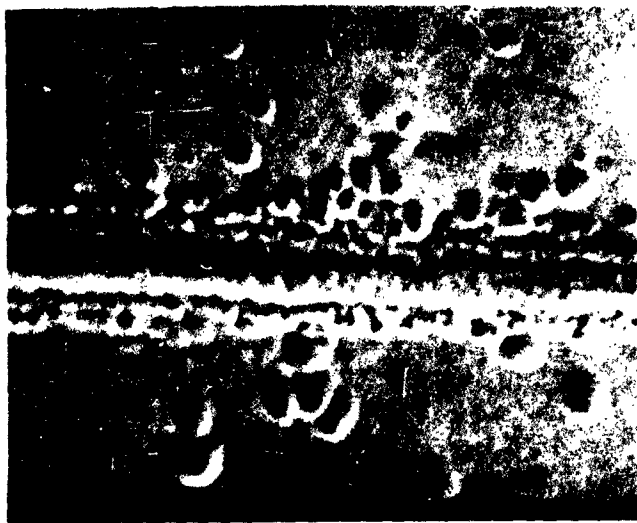

Fig. 19 Dislocation etch pits adjacent to a scratch on a (100) surface of a [100] whisker. Etched 15 minutes in 4 per cent picral
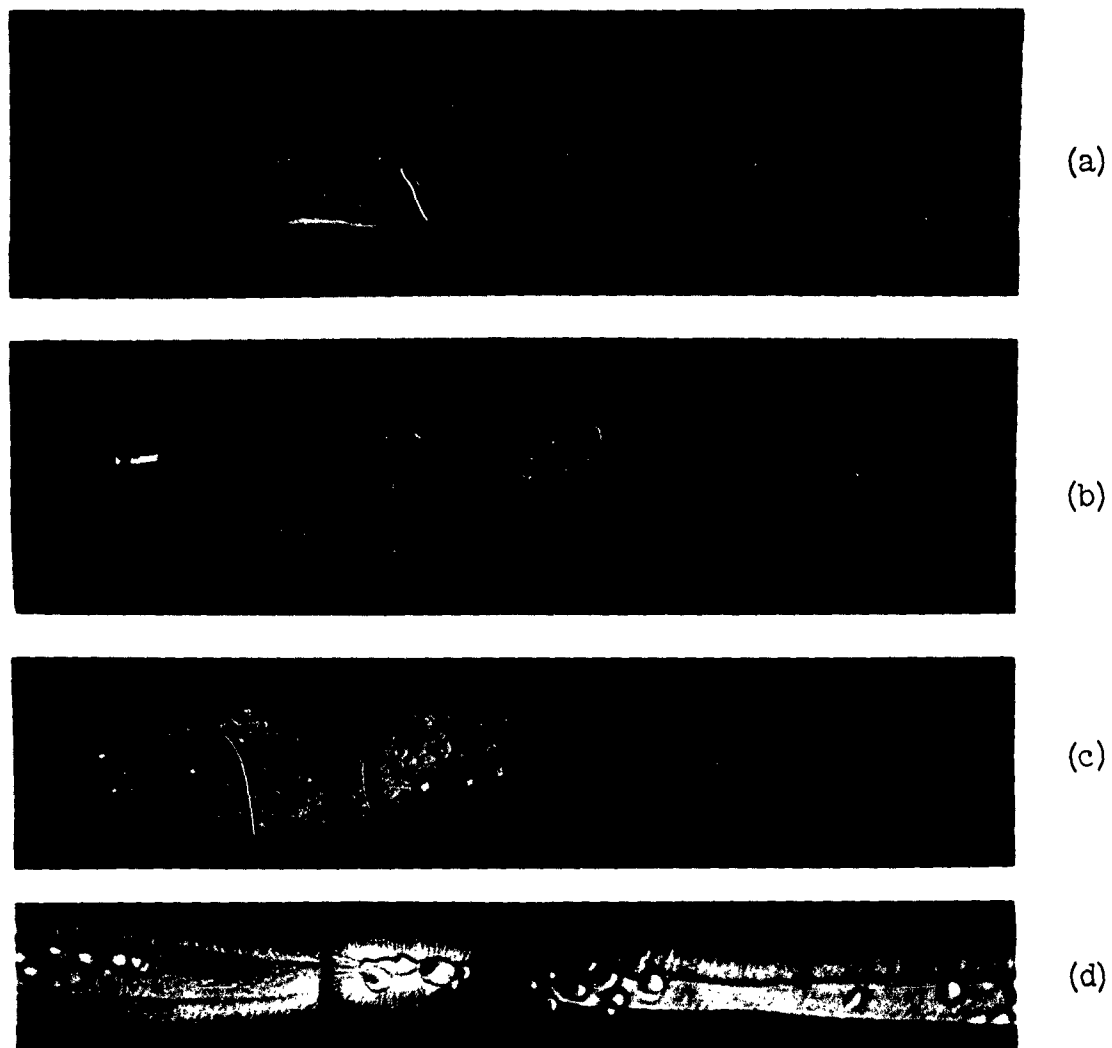1000X

Fig. 20 Etch pits near growth defect on a (100) surface of a [100] whisker. Etchant 4 per cent picral. (a) Not etched. (b) 5 minutes. (c) 15 minutes. (d) 30 minutes.   250X
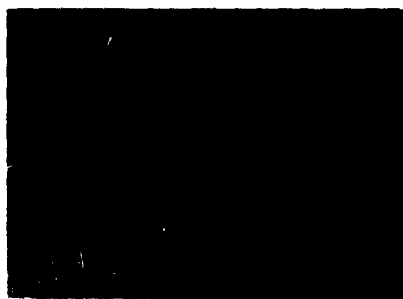
Fig. 21 Impurity segrega-
tion along a (100) whisker
axis. Etchant 4 per cent
picral for 30 minutes.
(Original magnification
1000X. Reduced to 50 per
cent.)

Fig. 22 Growth bend in a [110]
whisker. Surface of observa-
tion is (100) plane. Etched in
Fry's reagent for 5 seconds.
(Original magnification 150X.
Reduced to 50 per cent.)

Fig. 23 Etch pit shape as function of density on (100) surface.
Sample carburized, deformed, aged, and etched in electro-
lytic hydral.   500X

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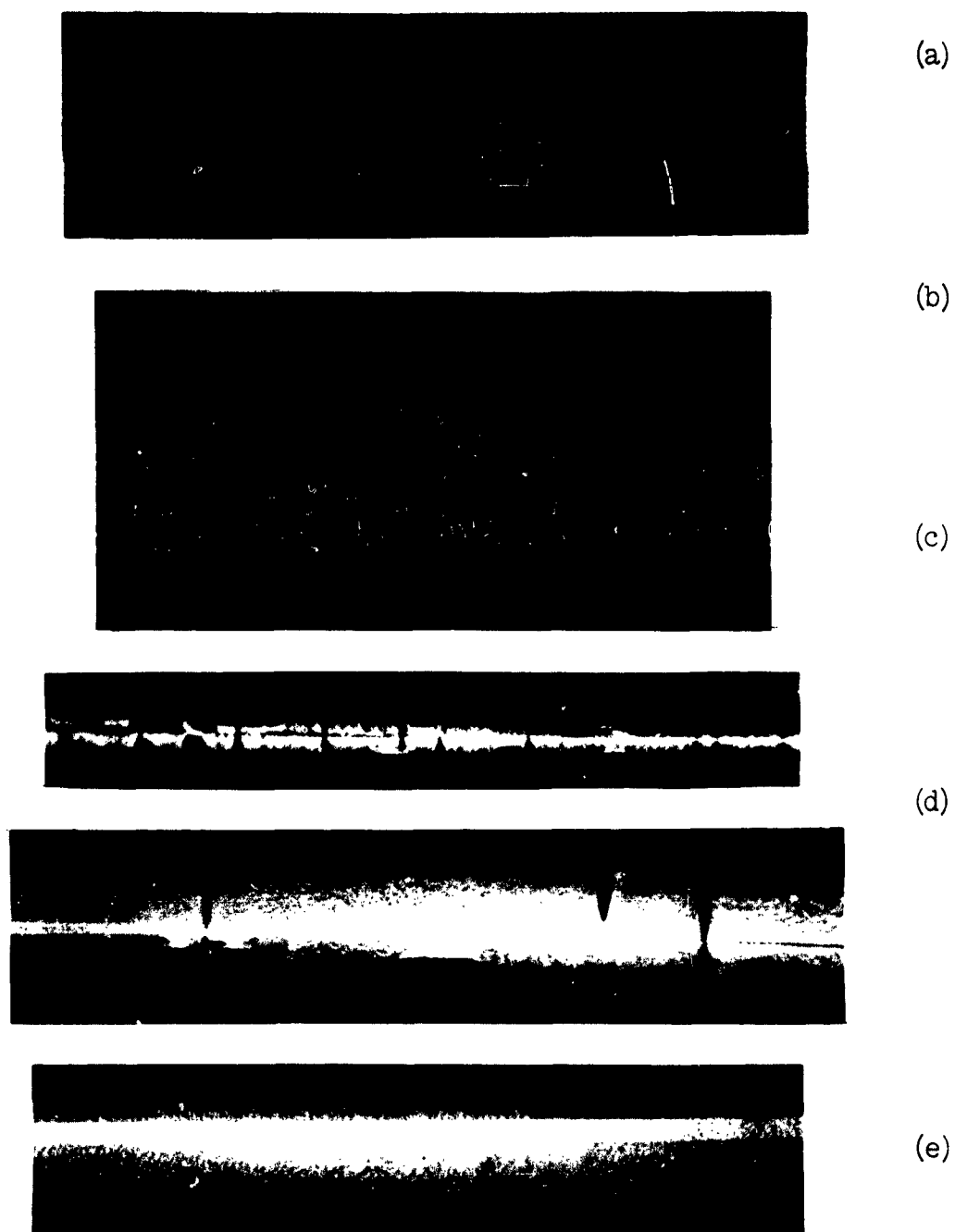
Fig. 24. Typical dislocation structure in [100] carburized and aged whiskers. (a) No dislocations. (b) A few dislocations in large whisker. (c) A few dislocations in small whisker. (d) Many random dislocations. (e) Variation in dislocation density along length of whisker. (Original magnifications (a), (b), and (c) 500X; (d) 1000X and (e) 400X. Reduced to 85 per cent.)
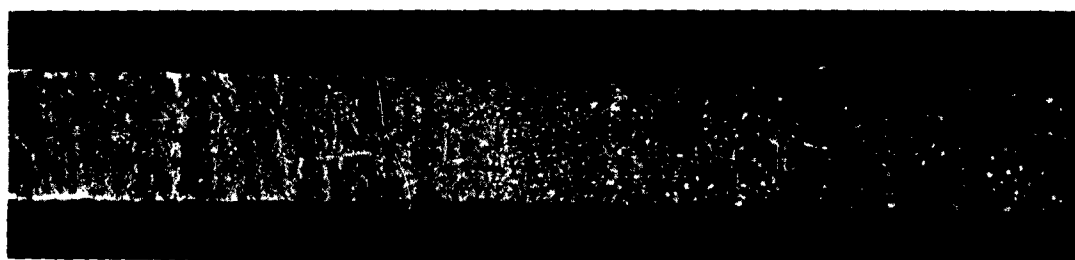
Fig. 25 Typical small-angle boundaries in [100] whiskers. (a) 1000X. (b) 1000X. (c) 400X.
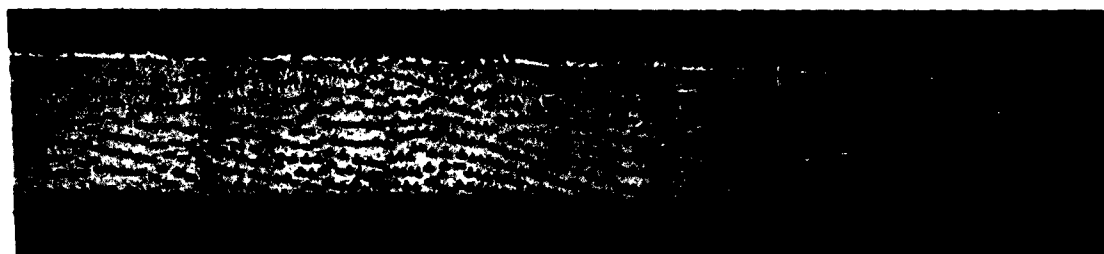
Fig. 26 Substructure resulting from damage near [100] whisker tips. (a) 250X. (b) 400X.

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(a)   (b)

Fig. 27 Low-angle boundary on tip and side surface of a [100] whisker. (a) Tip.
(b) Side.   500X

Fig. 28 Dislocation structure at intersection of
two [100] whiskers.   500X

Fig. 29   Polygonization on deformed and annealed [100] whisker.   500X

Fig. 30   Growth defect on [110]
   whisker. (Original magnification
   500X. Reduced to 55 per cent.)

Fig. 31   Polygonized structure in [110]
   whisker near intersection with second
   whisker. (Original magnification
   250X.   Reduced to 50 per cent.)

Fig. 32   Small-angle boundaries in
   deformed region of [110] whisker.
   (Original magnification 1000X.
   Reduced to 50 per cent.)

Fig. 33   Small-angle boundaries near
   growth defect on [110] whisker.
   (Original magnification 250X.
   Reduced to 50 per cent.)

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Fig. 34 Polygonization in deformed and annealed [110] crystal. (Original magnification 250X. Reduced to 63 per cent.)

Fig. 35 Dislocation etch pits in a [110] whisker at growth bend and associated with overgrowths. (Original magnification 250X. Reduced to 67 per cent.)

(a)

(b)

(c)
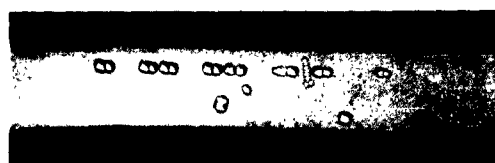
(d)

Fig. 36 Dislocation structure of typical [111] whiskers. (Original magnifications (a) and (b) 500X; (c) and (d) 250X. Reduced to 50 per cent.)

Fig. 37 Slip bands in a deformed [111] whisker.   250X

Fig. 38 Small-angle boundaries in [111] whisker near junction
with another whisker.   500X

Fig. 39 Overgrowth on a [111] whisker. Unetched.   250X

Fig. 40 Dislocation etch pits under overgrowth on a [111] whisker.
250X

Fig. 41 Flat-bottomed pitting on a [111] whisker.   500X

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PART III

ELECTRON TRANSMISSION MICROSCOPY OF IRON WHISKERS
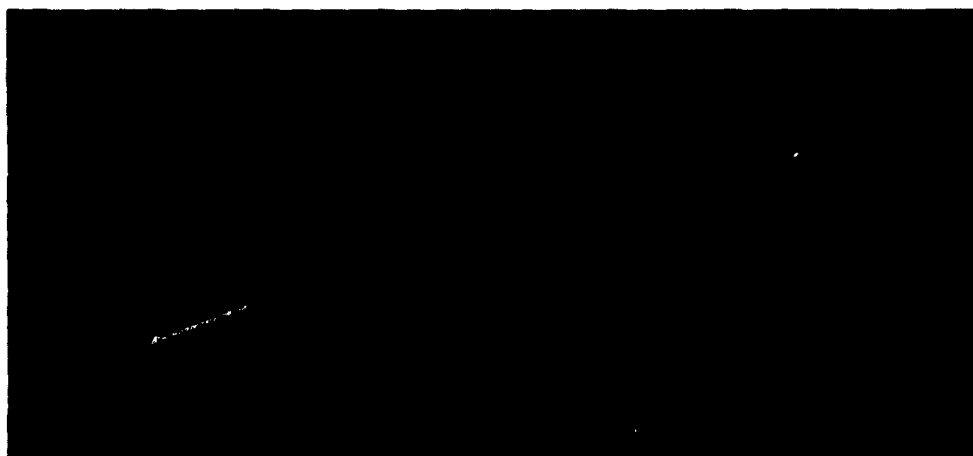
T. H. Alden

INTRODUCTION

Previous sections of this report have described the development of etching techniques for iron single crystals and the application of these techniques to the study of large iron whiskers. Although the evidence indicated that variation in dislocation structure existed and could explain the scatter in strength properties, it was not possible by this means to study whiskers less than 10 microns in diameter. Brenner[20] showed that in this size range a rapid increase in average strength occurs, inversely proportional to the whisker diameter.

The principal alternative method for revealing dislocations in metal crystals is that of thin film transmission electron microscopy.[28] The current maximum film thickness for this method is about 2500 A. Small whiskers approach this thickness in the as-grown condition, so that brief chemical thinning could produce suitable specimens. Despite the probable difficulties, such a program seemed worth while because of the importance of obtaining direct evidence on the defect structure of small whiskers.

An alternative approach was based on the idea that surface imperfections, e.g., surface steps, rather than internal arrays of dislocations, could lead to a reduction in strength.[20, 29] Recent photoelastic studies show that surface steps are severe stress concentrators.[30] Early in the study of whisker thinning, a polishing technique was developed which produced very smooth surfaces on small specimens. As a first approach, it was felt that comparison of the strengths of polished and unpolished whiskers would be worthwhile.[29]

EXPERIMENTAL METHODS

CHEMICAL THINNING OF WHISKERS

To thin the whiskers to the required 2500 A and still retain a reasonable width of specimen to examine, it is necessary to mask one or perhaps three sides of the whisker. A thermoplastic film, about 10 microns thick, on a substrate of glass or Mylar, was selected as a masking agent. The plastics are polystyrene and polymethyl methacrylate. These are dissolved in toluene, and in thin solution applied to the substrate. The whisker is laid on the film and the entire unit is

warmed to the softening temperature of the plastic. The whisker is drawn down and partially surrounded by the plastic during the warming operation. The precise shape of the plastic whisker interface, however, is not known.

Electrochemical and chemical thinning methods may be used. In all cases, the whisker is first embedded in thermoplastic. With the former, one whisker end is gripped with tweezers to make electrical contact and the assembly dipped into the electrolyte. The polishing treatment is:

Solution:

     80 grams CrO_3
    420 cc glacial acetic acid
    22.4 cc water

Conditions:

    18° to 19°C
    2.5 volts

This treatment is identical to that used for bulk iron except that 2.5 volts is used rather than 22.5 volts. Repeated polishing and microscopic examination are required to establish the necessary polishing time.

With the chemical solution (saturated picric acid in lauryl alcohol, $C_{12}H_{23}OH$) polishing is carried out at room temperature by placing a drop directly onto the masked whisker. The progress of the reaction may be directly viewed with the microscope. The chemical method is generally more satisfactory, being easier to control and producing more nearly the ideal blade shape. Thinning times are several hours for 2-micron whiskers and up to several days for 30-micron whiskers. Normally, only a portion of the end of the whisker is thin enough to transmit electrons.

The most difficult experimental problem is the handling of the very small thinned specimens and their attachment to the microscope grid. The most successful technique requires direct solution of the polystyrene in toluene, allowing a selected, cut portion of the thinned whisker to float free into a very small (less the 1 cm diameter) porcelain dish. The whisker fragment may then be observed at 30X while the dish is filled several times with clean toluene and finally, when dry, tapped out onto filter paper. A 100-mesh grid, previously covered with a thin coat of viscous fluid, "Vistac 4," by dipping in a toluene-thinned solution, is placed in proper position over the whisker fragment, and the two are gently rolled together with a flexible plastic tube. Finally, the whisker is sandwiched by the addition of a second 100-mesh grid.

Mechanical tests were made on the machine described by Brenner.[31] The whiskers tended to fail at or near the grips.

RESULTS

A number of thinned whiskers of size 2 to 4 microns and axis [100] were examined by transmission electron microscopy. All had the same general appearance (Fig. 42). Most regions showed strong extinction contours from the tapering of thickness toward the end and outside edge of the specimen. Spotty debris, observed to some degree in all specimens, is believed to be a reaction product of the thinning operation, probably iron picrate. An extreme case is shown in Fig. 43. Many regions showed a longitudinal striping possibly resulting from impurity introduced during growth from iron bromide. In no case were dislocations observed.

Fig. 42 Transmission electron micrograph of a 2-micron whisker. General view showing extinction contours and mottled contrast. (Original magnification 100,000X. Reduced to 50 per cent.)

Following the etch-pit work described earlier, it appeared that large whiskers (20 to 30 microns) were more likely to contain dislocations than small ones. With this in mind, many 30-micron specimens were thinned and several were examined. Unfortunately, the thinning technique was much less satisfactory here, the prolonged polishing times causing a severe rounding of the specimen surface. In most cases the extinction contours were so dark and closely spaced that little else could be distinguished. It was not possible to introduce dislocations by deforming the thinned whiskers using tweezer points or fine needles. Either the specimen deformed only elastically, or it became severely bent and could no

Fig. 43 Transmission electron micrograph. Debris, probably iron picrate, is particularly evident. (Original magnification 100,000X. Reduced to 50 per cent.)

longer be mounted in the microscope. Neither were efforts successful in isolating whisker kinks or other growth defects in a thinned condition.

Attempts to carry out mechanical testing of electropolished whiskers were unsuccessful. Because of the great difficulties in handling 1- to 5-micron whiskers and particularly in polishing prior to testing, later tests were confined to 8- to 12-micron specimens. It was soon discovered, in agreement with prior experience,[32] that a strong whisker in this size range almost always breaks free at the grips prior to failure. Repeated attempts to improve testing techniques were not successful in overcoming this problem.

CONCLUSION

If dislocations were present in the 2-micron whiskers, it is likely that they would have been observed. However, only a short region at the end of the thinned whisker is transparent. If, as was indicated by the etch-pit studies, dislocation densities are highly nonuniform, it is possible that the regions of high density were missed in all cases.

The question of the role of surface defects is unresolved. If electro-polished whiskers show higher average strengths than as-grown ones, then a portion of the defects must be at the surface. This experiment, however, tells nothing specific about the nature of the defects. As indicated earlier, dislocation densities may be higher at the surface. It is necessary to combine strength measurements with some more direct means of observing the defect structure of the whisker.

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